ERDC/TN SMART-04-6
September 2004

System-wide Modeling, Assessment, and Restoration Technologies

Variations in Field-Scale Nitrogen and Phosphorus Concentrations in Runoff as a Function of Land-Use Practice

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PURPOSE: The purpose of this research was to examine nitrogen and phosphorus concentrations in runoff at the field-scale level (i.e., homogeneous land-use plot) over a variety of land-use practices. Land-use practices included animal containment/barnyard areas, corn production fields, alfalfa and grass hayfields, Conservation Reserve Program (CRP) fields, and woodlots located in the upper Eau Galle River Watershed, west-central Wisconsin. The watershed is dominated by agricultural and dairy livestock land-use practices. Results from this study will be important in improving watershed modeling capabilities for predicting the runoff of nutrients from complex landscape mosaics.

BACKGROUND: Transformations and fluxes of nitrogen (N) and phosphorus (P) forms from the landscape are dictated by many complex factors including agricultural management practices, soil erosion and overland runoff potential, soil type, and soil nutrient concentration (Lemunyon and Gilbert 1993; Sharpley 1995). In particular, management of soils for crop production via fertilization and manure application can result in nutrient storage in the soil in excess of crop demand (particularly for P), leading to enhanced potential for soil nutrient loss during overland flow (Sims 1993; Sharpley et al. 1996) and accelerated eutrophication of receiving waters (Sharpley et al. 1994).

More information is needed regarding the impacts of land use and agricultural and dairy-livestock management on runoff N and P concentrations in order to improve predictive watershed modeling capabilities. For instance, Sharpley et al. (1991), Sharpley and Smith (1992), and Sharpley et al. (1992) found that NaOH-extractable P provided a quantifiable surrogate measure of the bioavailability of P in runoff. However, speciation of N and P concentrations into biologically labile (i.e., forms that are directly available for biological uptake or subject to recycling avenues that make it available) and refractory (i.e., forms that are not readily available for biological uptake and subject to burial) components via extraction techniques is still needed in order to better understand and predict the impact of nutrient runoff on biological uptake and growth in receiving waters (James et al. 2002). For P, labile components include soluble forms, loosely bound and iron-bound particulate P (i.e., subject to eH and pH transformations and equilibrium processes), and labile organic PP (Table 1). The latter form is susceptible to bacterial mineralization processes and also includes bacterial polyphosphates that can be recycled for biological uptake (Gächter et al. 1988; Jensen and Andersen 1992; Gächter and Meyer 1993; Hupfer et al. 1995). More refractory P forms include aluminum-bound, calcium-bound, and refractory organic particulate P (Hieltjes and Lijklema 1980; Penn et al. 1995). For N, both inorganic and organic forms can be recycled and used for biological uptake.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **SEP 2004**	2. REPORT TYPE	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Variations in Field-Scale Nitrogen and Phosphorus Concentrations in Runoff as a Function of Land-Use Practice**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Army Engineer Research and Development Center,Environmental Laboratory,3909 Halls Ferry Road,Vicksburg,MS,39180-6199**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT
see report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**21**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Table 1
Operationally Defined Phosphorus Fractions

Variable	Extractant	Biological Availability and Susceptibility to Recycling Pathways
Loosely-bound P	1 M ammonium chloride	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Iron-bound P	0.11 M sodium bicarbonate-dithionate	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Aluminum-bound P	0.1 N sodium hydroxide	Biologically refractory; generally unavailable for biological use and subject to burial.
Calcium-bound P	0.5 N hydrochloric acid	Biologically refractory; generally unavailable for biological use and subject to burial.
Labile organic/ polyphosphate P	Persulfate digestion of the NaOH extraction	Biologically labile; polyphosphates are available for biological uptake. Also recycled via bacterial mineralization and surplus storage in cells.
Refractory organic P	Persulfate digestion of remaining particulate P	Biologically refractory; generally unavailable for biological use and subject to burial.

Note: Labile = Subject to recycling pathways or direct availability to the biota.
Refractory = Low biological availability and subject to burial.

The objectives of this study were to examine runoff concentrations of various N and P species from fields over different land-use categories in order to determine possible relationships between runoff concentrations and the extent of soil management. N and P were also partitioned into biologically labile and refractory components of the runoff for examination of the potential susceptibility of runoff concentrations to eutrophication of receiving waters.

METHODS: Runoff collection devices (RCDs) were designed to capture a sample of field runoff; they were not equipped to measure runoff flow or volume. RCD construction is shown in Figure 1. PVC schedule 40 piping (3 m in length by 4 cm in diameter) was slotted at 15-cm intervals to capture field runoff. The pipes were deployed in the field to form an ~ 120-deg angle perpendicular to the field's slope (~6 m of exposure). A screen (2-mm mesh) was wrapped around each PVC pipe to prevent entrance and clogging by large particulate material. Tubing attached to nipples protruding out of the capped inner ends of the PVC pipe directed runoff to an acid-washed polyethylene bottle (2 L), which was deployed in a hole located at the conjunction of the two PVC pipes. The sample bottle was capped and contained a port for attachment of the collection tubing. The bottle was secured in the hole by a stake to prevent floating in the event of flooding. PVC pipes were secured in place by stakes and sand-filled bags (5-cm diam) that were placed behind each PVC pipe.

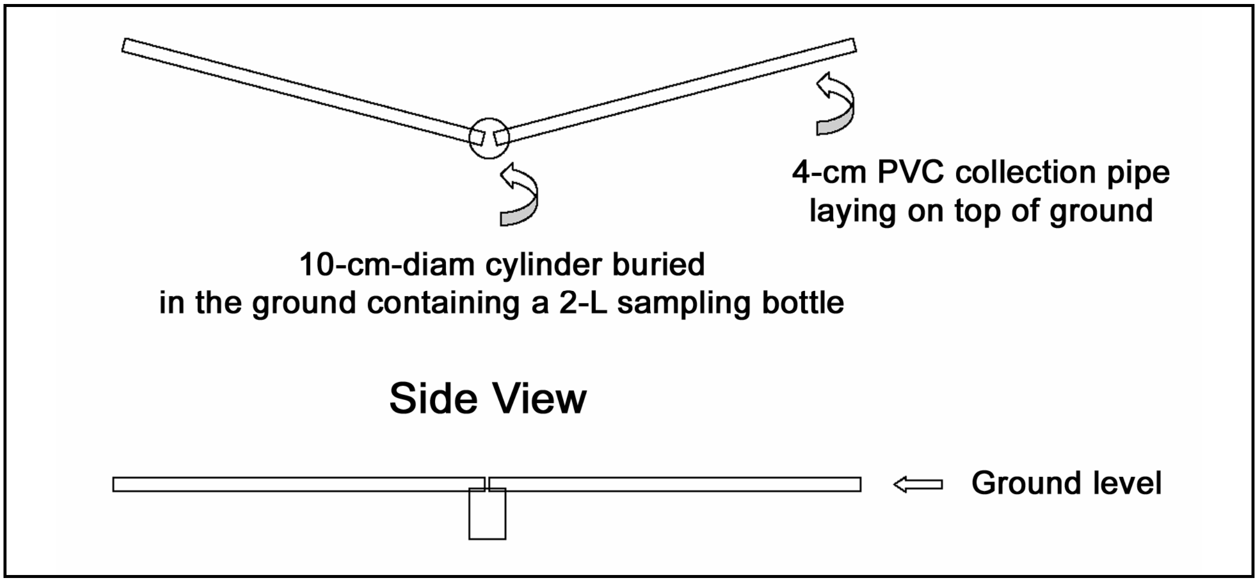

Figure 1. Runoff collection device

RCDs were placed in fields containing a homogeneous land-use practice located within the upper Eau Galle River watershed, a 166-km^2 watershed located in west-central Wisconsin (see James et al. (2003a) for a description of the watershed). RCDs were positioned in land-use fields with slopes ranging between 2 and 8 percent grade. An RCD was placed in three animal containment (barnyard) areas, five cornfields, two CRP fields, four hayfields (alfalfa or grass), and two woodlots. The total numbers of runoff events captured from each land-use area are shown in Table 2. Tipping bucket precipitation gauges (Dataloggers, Inc; Model S-162), placed in seven locations throughout the Eau Galle River watershed, monitored rainfall over 15-min intervals during RCD deployment.

Table 2
Runoff Events Captured in Each Land-Use Area

Land Use	Number of Runoff Events
Barnyards	22
Cornfields	36
Hay (Alfalfa and Grass)	11
CRP	18
Woodlots	13

In the laboratory, a portion of the runoff was filtered through a 0.45-µm filter for soluble constituent determination. Soluble reactive P (SRP), ammonium-N (NH_4-N), and nitrate-nitrite-N (NO_3NO_2-N) was analyzed using automated analytical techniques (Lachat Quikchem Autoanalyzer, Zellweger Analytics, Lachat Div., Milwaukee, WI). Total soluble N and P were analyzed colorimetrically using Lachet QuikChem procedures following digestion with alkaline potassium persulfate according to Ameel et al. (1993). For particulate components, sample aliquots were retained on glass fiber filters (Gelman Metricel; 2-µ nominal pore size). For total suspended solids (TSS) and particulate organic matter (POM), suspended material was dried at 105°C to a constant weight, then ignited at 500 °C in a muffle furnace (American Public Health Association (APHA) 1998). Sequential fractionation of inorganic particulate P (PP) in the sediments was conducted according to Hieltjes and Lijklema (1980), Psenner and Puckso (1988),

and Nürnberg (1988) for the determination of ammonium-chloride-extractable P (i.e., loosely bound PP), bicarbonate-dithionite-extractable P (i.e., iron-bound PP), sodium hydroxide-extractable P (i.e., aluminum-bound PP), and hydrochloric acid-extractable P (i.e., calcium-bound PP). Each extraction was filtered through a 0.45-µm filter, adjusted to pH 7, and analyzed for SRP using the ascorbic acid method (APHA 1998). A subsample of the NaOH extract was digested with potassium persulfate to determine nonreactive NaOH-extractable P (Psenner and Puckso 1988). Labile organic PP was calculated as the difference between reactive and nonreactive NaOH extractable P. PP remaining on the filter after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid to determine refractory organic PP. Samples for total N and P were predigested with alkaline potassium persulfate (Ameel et al. 1993) before analysis using automated analytical procedures. Particulate organic nitrogen (PON) was calculated as the difference between total and total soluble nitrogen. Soluble organic nitrogen (SON) was calculated as total soluble nitrogen minus the sum of NH_4-N and NO_3NO_2-N.

To measure P sorption characteristics of TSS from the runoff samples, the remaining sample was centrifuged at 500 g and decanted to separate the particulate from soluble phases. Sorption characteristics were determined on TSS collected from individual storms over the summer period from the RCDs for statistical evaluation. Enough TSS mass was collected during precipitation events from barnyard, cornfield, and woodlot sites only for adsorption-desorption analysis. TSS mass was too low for examination of equilibrium characteristics from other land uses (i.e., hay and CRP). Sediment aliquots (~500 mg/L dry weight equivalent) were subjected to a series of SRP (KH_2PO_4 as SRP) standards ranging from 0 to 1.0 mg/L (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg/L) for examination of P adsorption and desorption over a 24-hr period. This high solute:TSS ratio (2000:1) was used to simulate concentrations and sorption characteristics of the TSS concentrations typically observed in tributaties of the Eau Galle watershed. Untreated tap water from the laboratory was used as the water medium because it was phosphate-free and exhibited very similar cationic strength, conductivity, and pH to that of surface water from the Eau Galle River. Chloroform (0.1 percent) was added to inhibit biological activity. The sediment systems, containing sediment, tap water, and known concentrations of SRP, were shaken uniformly for 24 hr and then sampled and analyzed for SRP (APHA 1998). The sediment systems were maintained under oxic conditions at a pH of ~ 8.0 to 8.3 and a temperature of ~ 20 ^oC .

The change in SRP mass (i.e., initial SRP - final SRP; mg) over the 24-hr period was divided by the dry mass equivalent of TSS used in the experiment to determine the quantity of P desorbed or adsorbed (mg P kg^{-1} TSS). These data were plotted as a function of the equilibrium SRP concentration after 24 hr of incubation to determine the linear adsorption coefficient (K_d; L kg^{-1}), the equilibrium P concentration (EPC; mg P L^{-1}; the point where net sorption is zero), and the native adsorbed P (S_o; mg P kg^{-1} TSS; initial P adsorbed to the TSS). The K_d and S_o were calculated via regression analysis as the slope and the y-intercept, respectively, from linear relationships between final SRP concentrations and the quantity of P sorbed at low equilibrium concentrations (Pant and Reddy, 2001). The EPC was calculated as S_o divided by K_d.

As part of another study, soil samples were collected in the various land uses throughout the Eau Galle River watershed for examination of relationships between management and soil N and P

concentrations. Methodology and results are reported in James et al. (2004b). However, some of the information in that document was compared with runoff concentrations determined using the RCDs. Three replicate soil samples from the same land-use categories used in runoff concentration analysis were collected from the upper 5-cm horizon and composited into one sample. These soil samples were analyzed for Mehlich-3 P (Mehlich 1984) and total P (Plumb 1981).

RESULTS:

Phosphorus. Several precipitation events occurred in the watershed over the summer period (Figure 2). Daily precipitation exceeded 25 mm on 11 days and 50 mm on 2 days. Storm frequency was greatest in early May and early to mid-June. Conditions were much drier in late June through early August. Stronger storms, exceeding 25 mm, occurred in mid- and late August and early September.

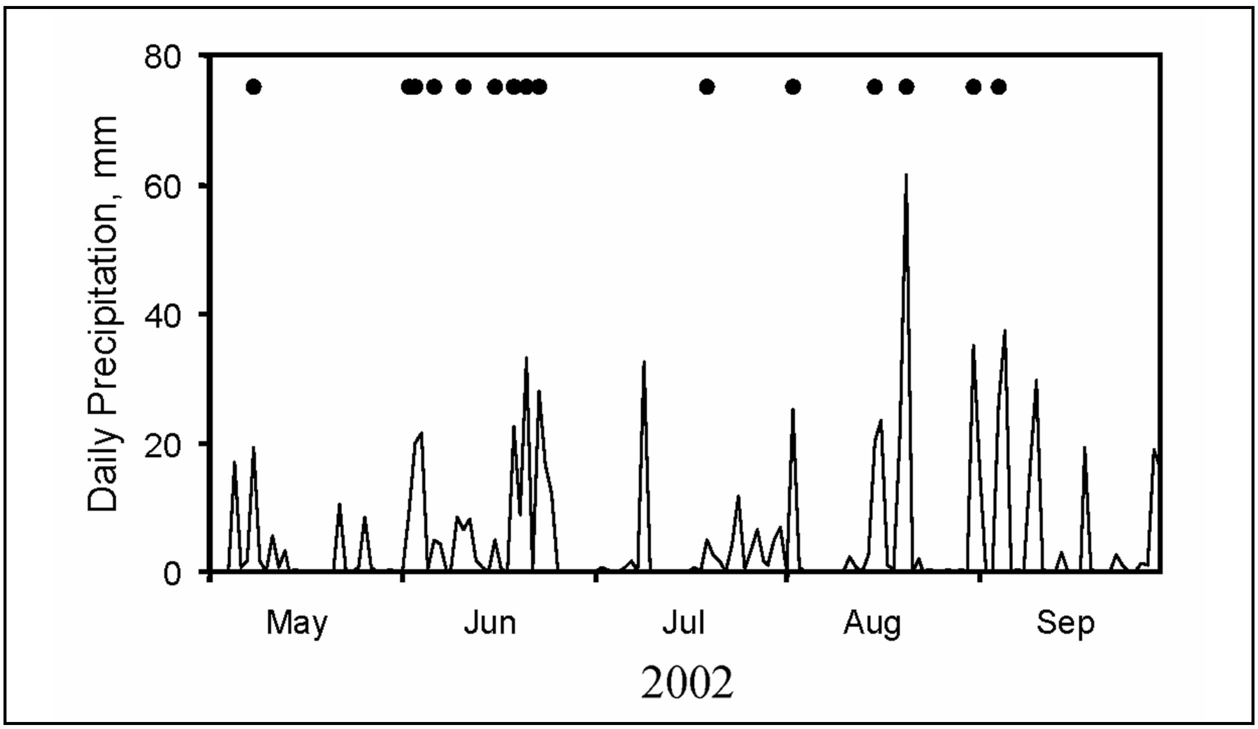

Figure 2. Daily precipitation over the Eau Galle Watershed between May and September 2002 (solid circles indicate periods of sample collection using the runoff collection devices)

P concentrations (mg L^{-1}) and composition (mg g^{-1}) varied among the different land-use practices. In general, mean concentrations of total P in the runoff were greatest from barnyards followed by corn ≥ alfalfa ≥ woodlots ≥ grass hay ≥ CRP (Figure 3). P concentrations in the runoff from barnyards, alfalfa hay, grass hay, and CRP were composed of predominantly soluble P (Figure 4). In contrast, particulate P forms comprised most of the P runoff from cornfields and woodlots. Thus, particulate P:soluble P ratios in the runoff were very high for woodlots and cornfields (23:1 and 26:1, respectively) compared to barnyards, alfalfa and grass hay, and CRP land uses (range = 0.1:1 to 1:1).

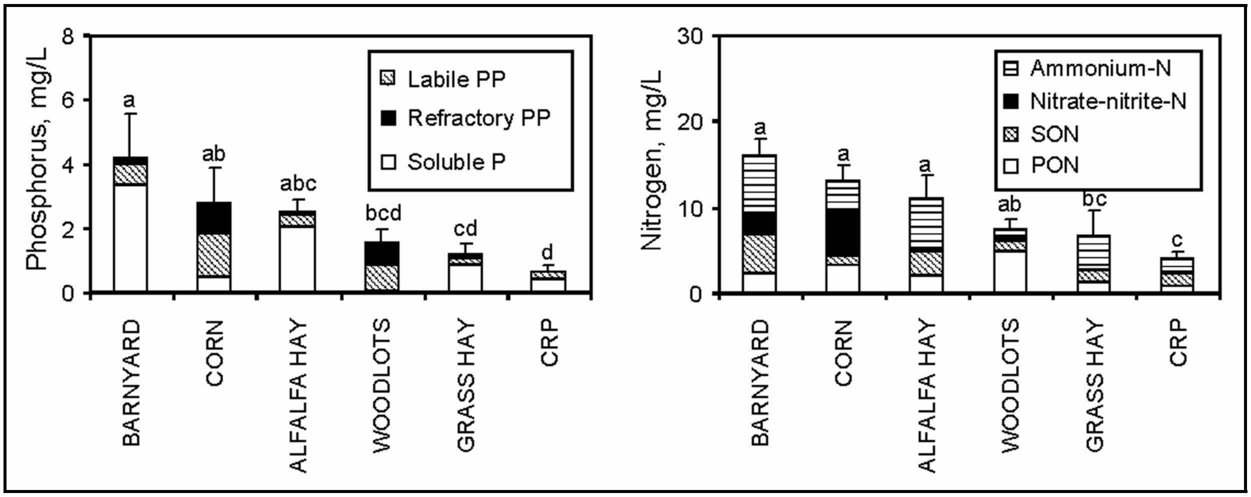

Figure 3. Variations in mean nitrogen and phosphorus concentrations in the runoff of various land uses. Mean labile particulate phosphorus (PP) represents the sum of loosely bound, iron-bound, and labile organic P fractions; mean refractory PP represents the sum of aluminum-bound, calcium-bound, and refractory organic P fractions; SON = soluble organic nitrogen; PON = particulate organic nitrogen. Vertical lines represent 1 standard error of the mean total N or P concentration. Letters above the means represent significant differences based on Duncan-Waller ANOVA

Overall, runoff from barnyards exhibited the greatest concentrations of biologically labile P (both soluble and particulate forms) followed by alfalfa, corn, grass hay, woodlots, and CRP (Figure 5). Refractory P concentrations were greatest in the runoff from cornfields, followed by woodlots, barnyards, alfalfa, grass hay, and CRP. However, refractory P concentrations were lower than labile P concentrations in the runoff from all land uses.

There were some strong positive linear relationships between total PP and labile PP mass-weighted composition (i.e., mg g^{-1}) over all land-use categories, suggesting a general trend of increasing labile PP composition as total PP concentration increased in the runoff (Figure 6). In particular, variations in total PP accounted for 87 percent of the variation in loosely bound PP. Significant linear relationships also existed between total PP and the iron-bound and labile organic PP fraction. When barnyards were excluded from the dataset, a strong linear relationship existed between the loosely bound PP fraction and concentrations of soluble P in the runoff over all other land-use categories (Figure 7), suggesting possible equilibrium control of soluble P concentrations by particulate phases in the runoff. However, linear relationships were not observed between soluble P and other labile PP fractions. Mass-weighted composition of these fractions was also much lower for these fractions compared to the loosely bound PP fraction (Figure 7). On an individual land-use basis, correlations between the loosely bound P concentration and soluble P in the runoff were strongest for cornfields ($p < 0.05$; Statistical Analysis System (SAS) Institute1994). In contrast, barnyards appeared to be skewed toward much higher soluble P concentrations at similar particulate P mass-weighted composition.

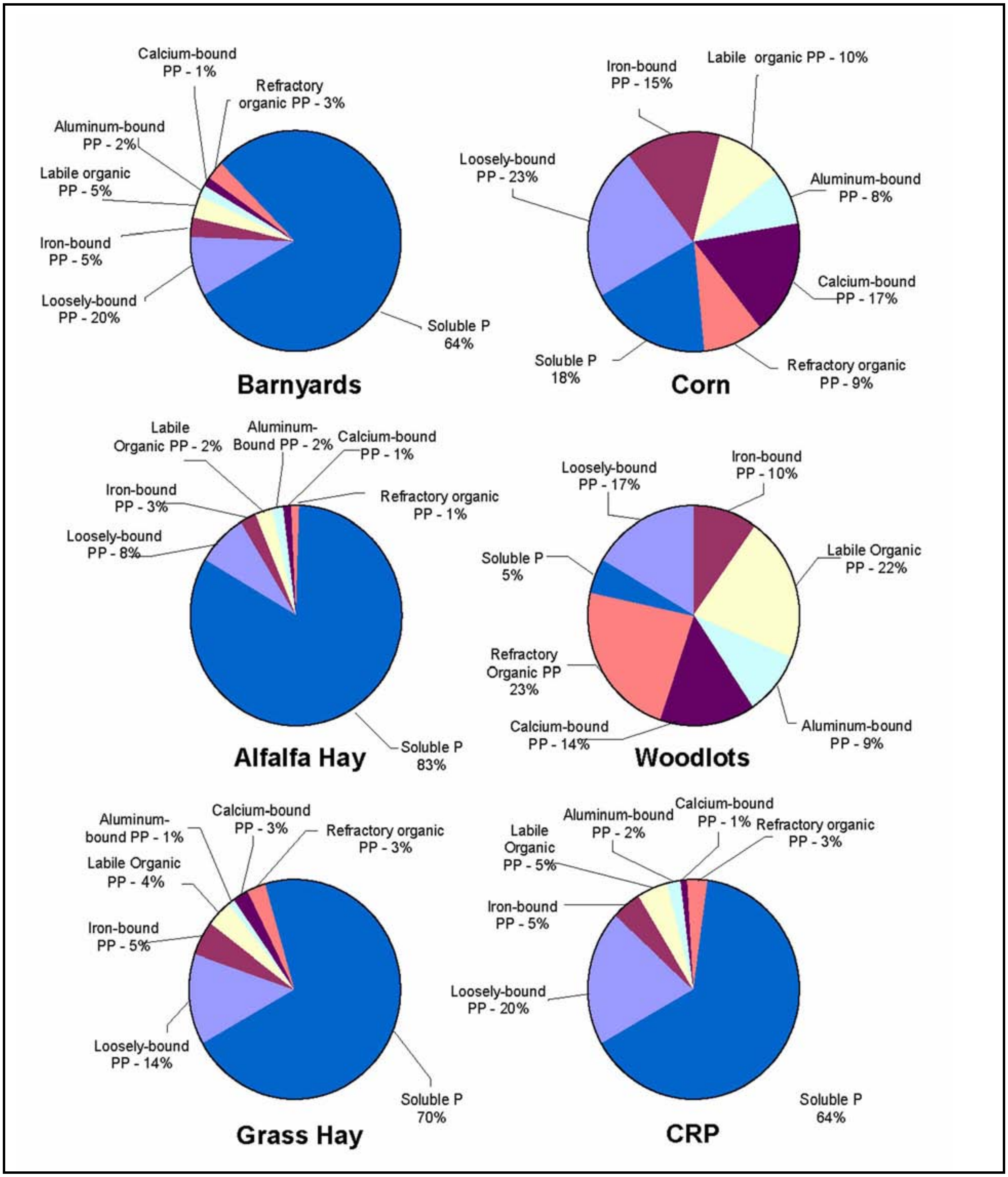

Figure 4. Variations in the mean composition of total phosphorus (P; percent) in the runoff as a function of land use (PP = particulate phosphorus)

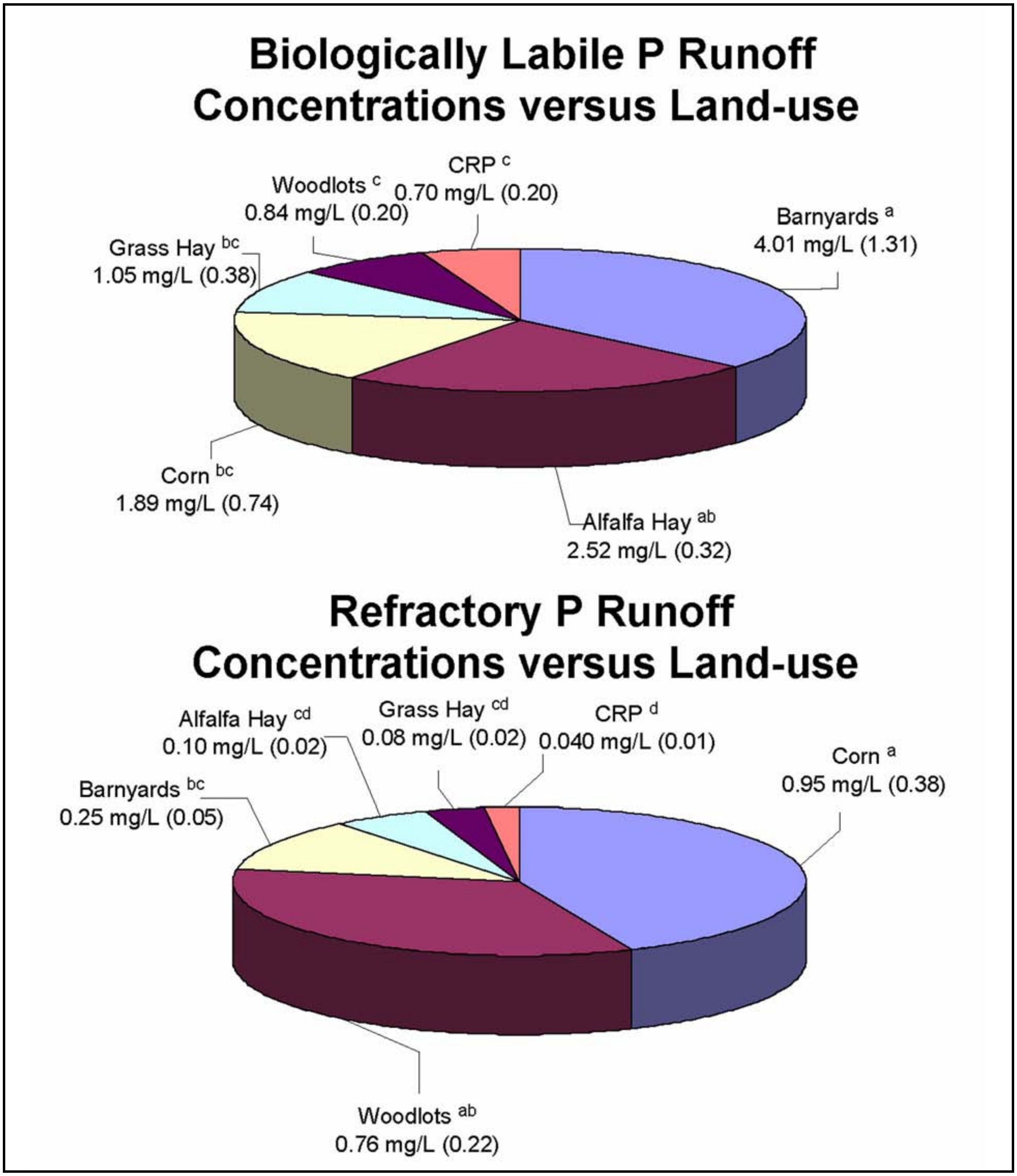

Figure 5. Variations in the mean composition of biologically labile (upper) and refractory phosphorus (P) as a function of land use. Labile P includes soluble P, loosely bound particulate P (PP), iron-bound PP and labile organic PP fractions. Refractory P includes aluminum-bound, calcium-bound, and refractory organic PP fractions. Numbers in parentheses represent 1 standard error. Letters above the means represent significant differences based on Duncan-Waller ANOVA

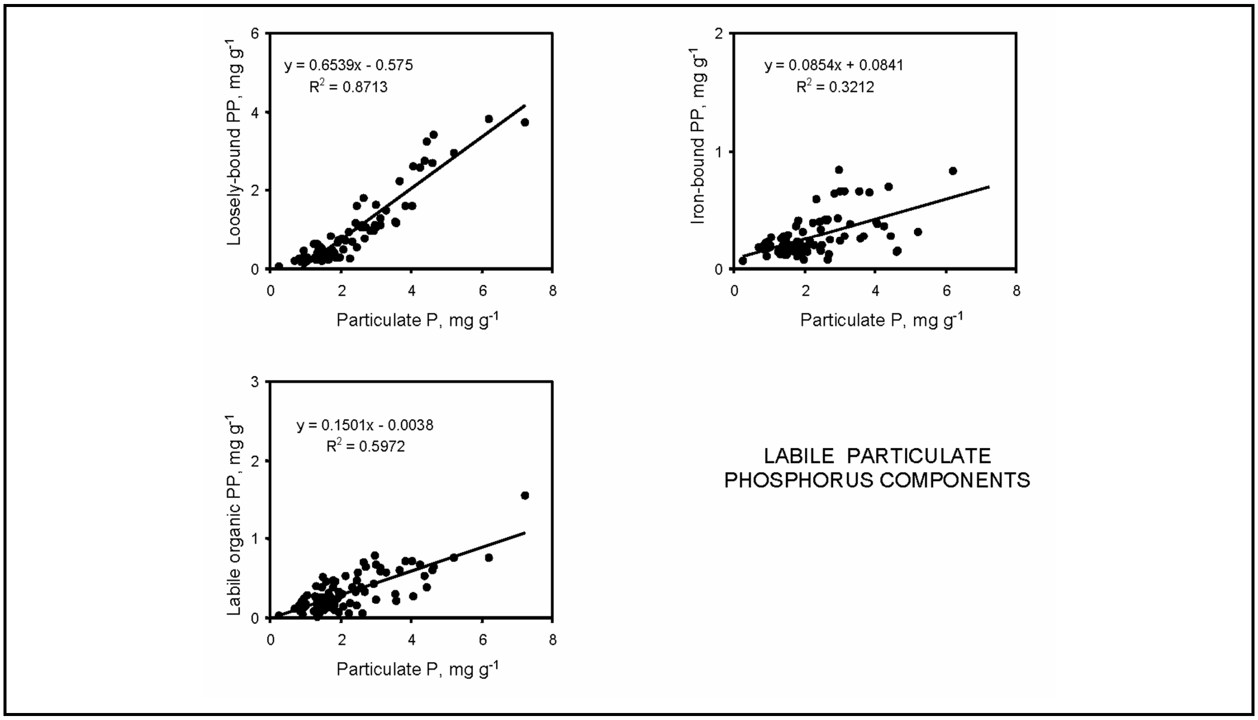

Figure 6. Linear relationships between particulate phosphorus (PP) and the loosely bound, iron-bound, and labile organic PP fractions over all land-use categories (significant relationships ($p < 0.05$) are represented with linear equations and r^2)

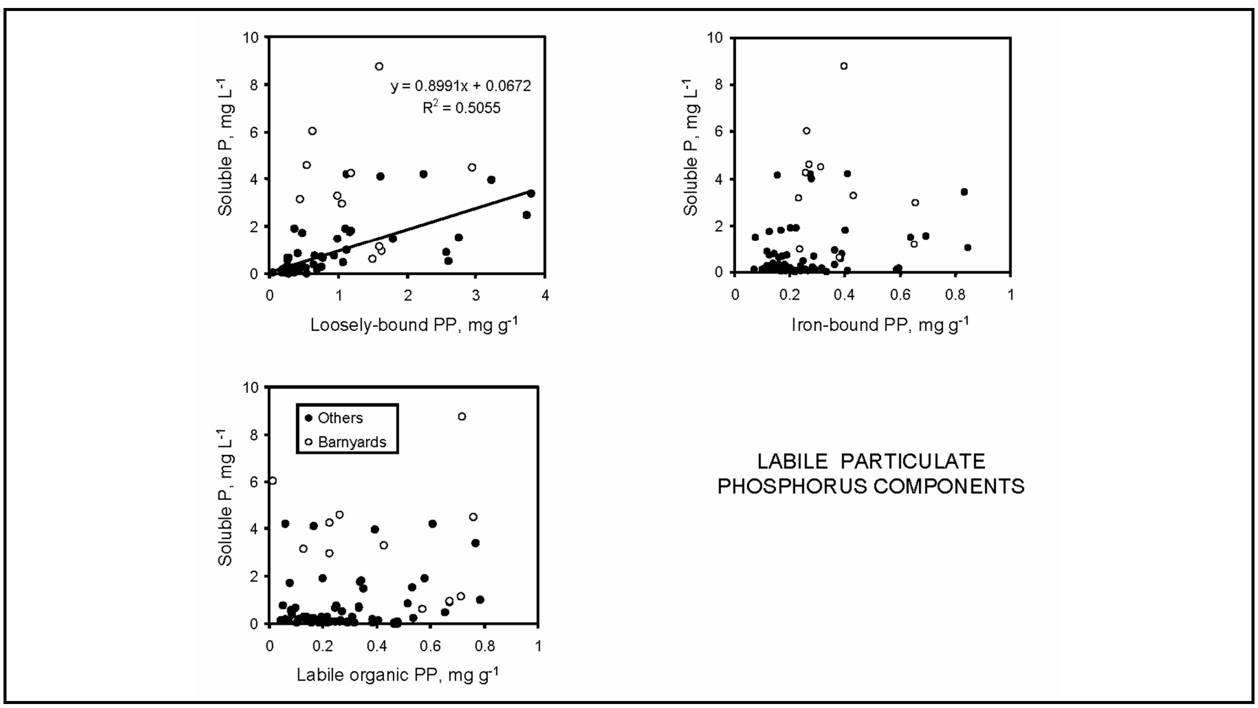

Figure 7. Linear relationships between loosely bound, iron-bound, or labile organic particulate phosphorus (PP) and soluble P over all land-use categories (significant relationships ($p < 0.05$) are represented with linear equations and r^2 after exclusion of barnyards from the analysis (see text for explanation))

With the exception of aluminum-bound PP, linear relationships between total PP and refractory PP mass-weighted composition were nonexistent (Figure 8). These refractory PP components were also not significantly related to soluble P concentrations over all land-use categories (Figure 9) or individual land-use patterns.

Marked and significant differences in the sorption characteristics of TSS in the runoff were observed as a function of different land-use categories (Figure 10). TSS from barnyard runoff exhibited P desorption at all 24-hr P equilibrium concentrations lower than ~ 0.6 mg L^{-1}. In contrast, P adsorption occurred at all 24-hr P equilibrium concentrations greater than 0.05 mg L^{-1} for TSS from woodlot runoff. Patterns for TSS from cornfields fell between those of barnyards and woodlots.

Barnyard TSS runoff exhibited the greatest mean EPC and S_o, followed by TSS runoff from cornfields and woodlots (Table 3; Figure 11). Mean K_d exhibited an opposite trend, as it was greatest for TSS in the runoff from woodlots, followed by TSS in the runoff from cornfields and barnyards. Trends in the mean mass-weighted composition of loosely bound and iron-bound PP (i.e., readily exchangeable particulate P) as a function of land-use practice, were similar to those for mean EPC and $S_{o,}$ suggesting relationships between readily exchangeable PP mass-weighted concentrations and P sorption characteristics. Linear relationships also existed between readily exchangeable P and the EPC (r^2=0.51) and the S_o (r^2=0.39 for each relationship; not shown).

Regression analysis (ln:ln) of mean Mehlich-3 soil P concentration (mg g^{-1}) versus mean soluble P (mg L^{-1}) and labile P (mg L^{-1}; includes labile PP and SP forms) runoff concentrations and mean total soil P (mg g^{-1}) versus mean labile particulate P (mg L^{-1}) from different land uses are shown in Figure 12. Mean concentrations of soluble and labile P in the runoff increased with increasing mean Mehlich-3 soil P concentration, suggesting relationships between crop-available P in the soil and labile forms of P in the runoff. However, relationships between total soil P and labile particulate P concentrations in the runoff were not observed.

Nitrogen. Total N runoff concentrations also varied as a function of land use, as they were greatest for barnyards, corn and alfalfa, followed by lower concentrations from woodlots, grass hay, and CRP (Figure 2). With the exception of runoff concentrations from woodlots, soluble forms of N followed a similar trend versus land use as total N. Eighty-six percent of the barnyard N runoff concentration was composed of soluble N species and NH_4-N was the dominant soluble N form (Figure 13). While N runoff concentration from cornfields was also composed of predominantly soluble forms (75 percent), the dominant soluble N species was NO_3NO_2 -N. Alfalfa, grass hay, and CRP N runoff concentrations were also composed primarily of NH_4-N. In contrast, PON comprised most of the N runoff concentration from woodlots.

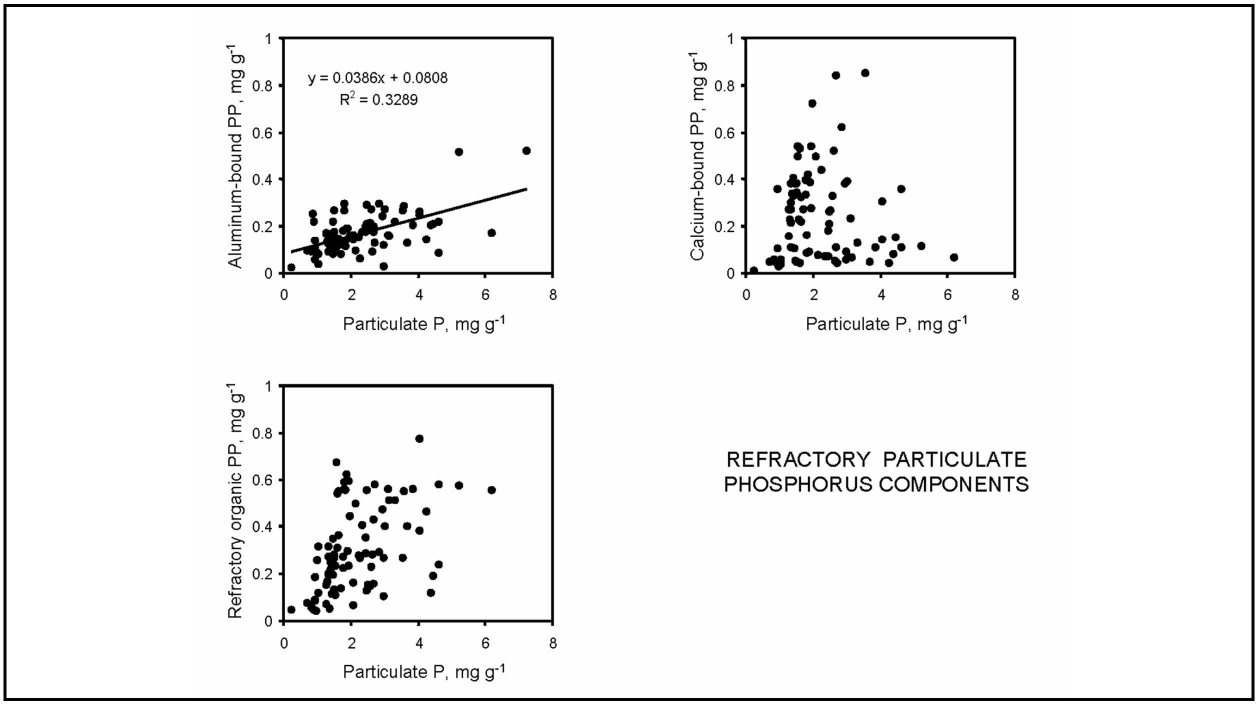

Figure 8. Linear relationships between particulate phosphorus (PP) and the aluminum-bound, calcium-bound, and refractory organic PP fractions over all land-use categories (significant relationships ($p < 0.05$) are represented with linear equations and r^2)

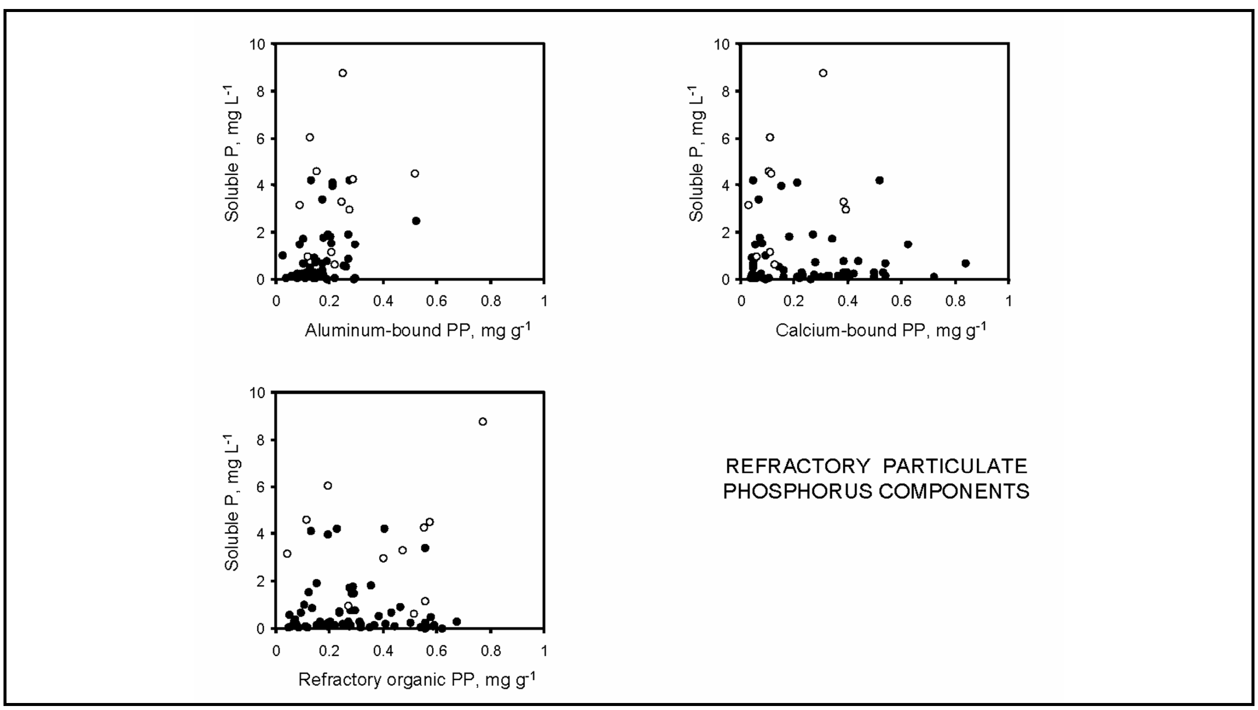

Figure 9. Aluminum-bound, calcium-bound, or refractory organic particulate phosphorus (PP) versus soluble P over all land-use categories. No significant relationships ($p < 0.05$) were found after exclusion of barnyards from the analysis (see text for explanation)

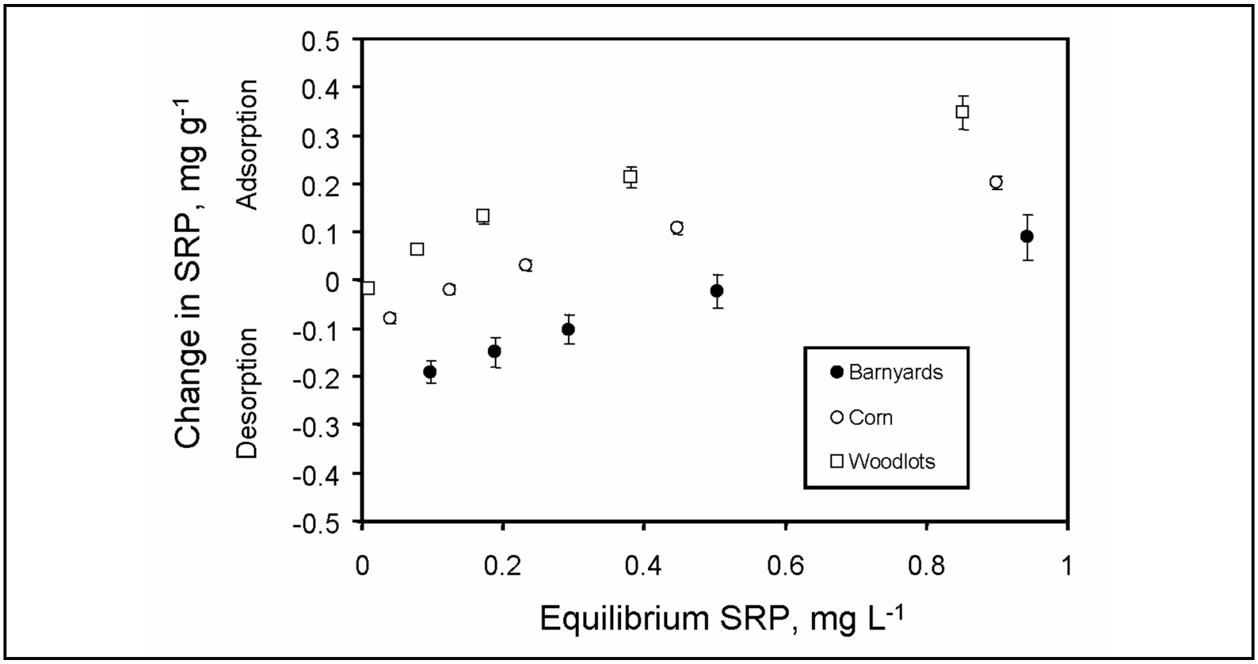

Figure 10. Mean sorption characteristics for total suspended solids (TSS) collected from the runoff of barnyards, corn production fields, and woodlots. Equilibrium soluble reactive phosphorus (SRP) represents the aqueous P concentration after 24 hr of contact with TSS (500 mg L^{-1}). A positive change in SRP represents adsorption of aqueous P onto TSS, while a negative change in SRP represents desorption of P from TSS into aqueous phases. Vertical lines represent 1 standard error of the mean

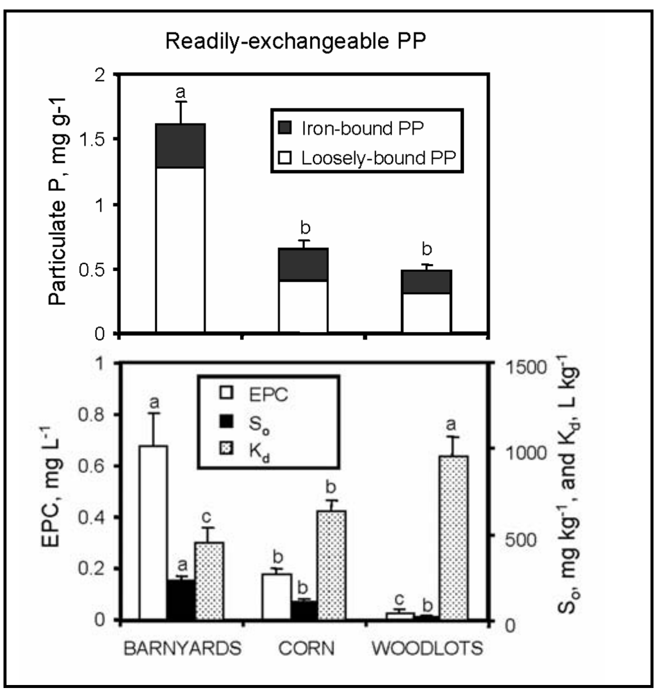

Figure 11. Variations in mean readily exchangeable particulate phosphorus (PP), the equilibrium phosphate concentration (EPC), the native adsorbed P (S_o), and the linear adsorption coefficient (K_d) for barnyard, corn production field, and woodlot land uses. Readily exchangeable PP represents the sum of the loosely bound and iron-bound PP fraction. Vertical bars represent 1 standard error. Letters above the means represent significant differences based on Duncan-Waller ANOVA

Table 3
Mean (1 Standard Error in Parentheses) Equilibrium Phosphorus Concentration (EPC), Native Adsorbed P (S_o), and Linear Adsorption Coefficient (K_d) for TSS Collected in the Runoff of Barnyards (n=10), Cornfields (n=32), and Woodlots (n=11)

Land Use	EPC, mg L^{-1}	S_o, mg kg^{-1}	K_d, L kg^{-1}
Barnyards	0.674 (0.129)	230 (30)	451 (85)
Cornfields	0.179 (0.022)	107 (20)	633 (62)
Woodlots	0.026 (0.013)	20 (8)	950 (121)

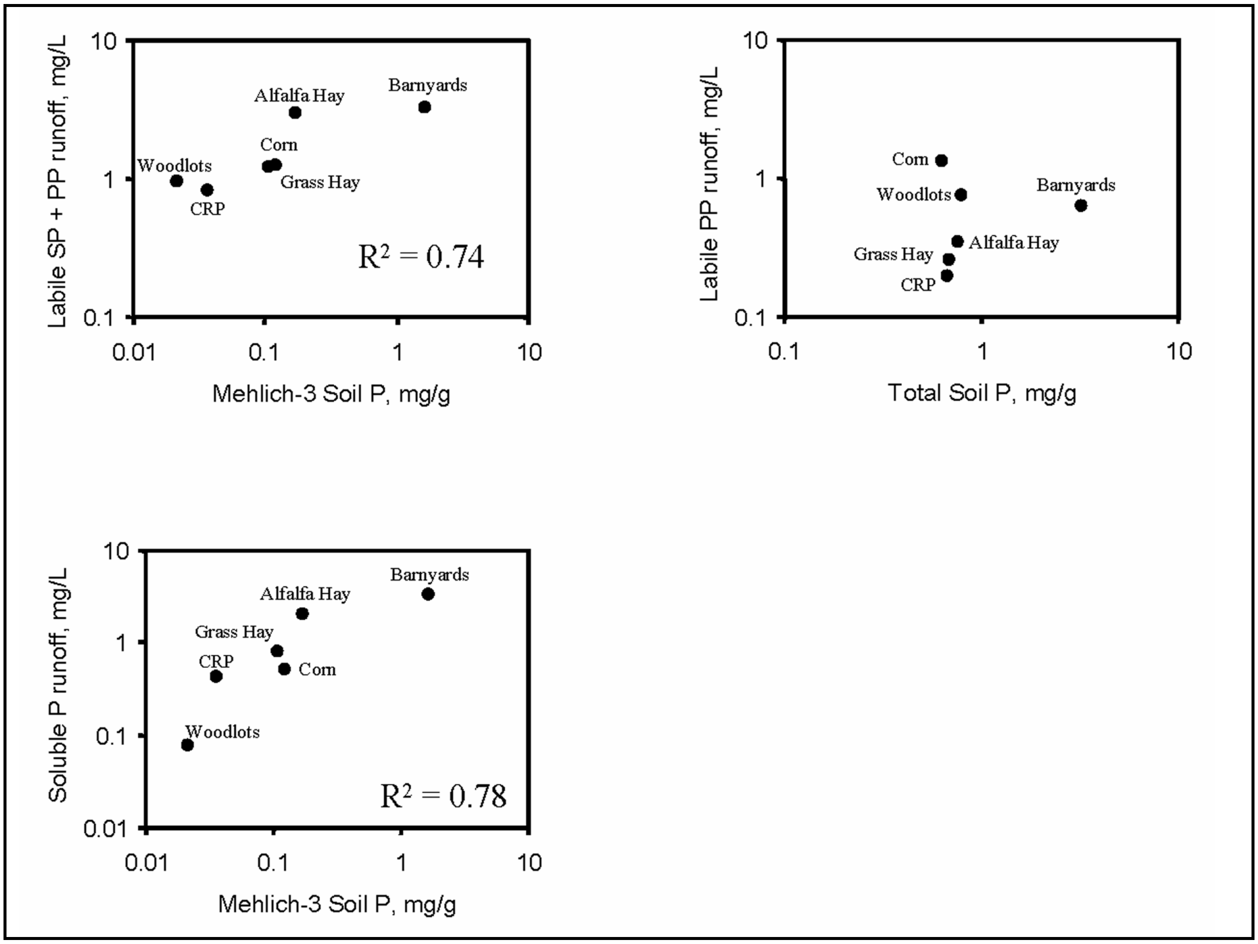

Figure 12. Mean Mehlich-3 soil test P or mean total soil P versus mean labile phosphorus (P; i.e., the sum of soluble P, and the loosely bound, iron-bound, and labile organic particulate P fractions). Significant linear relationships ($p < 0.05$) are indicated with the r^2 value

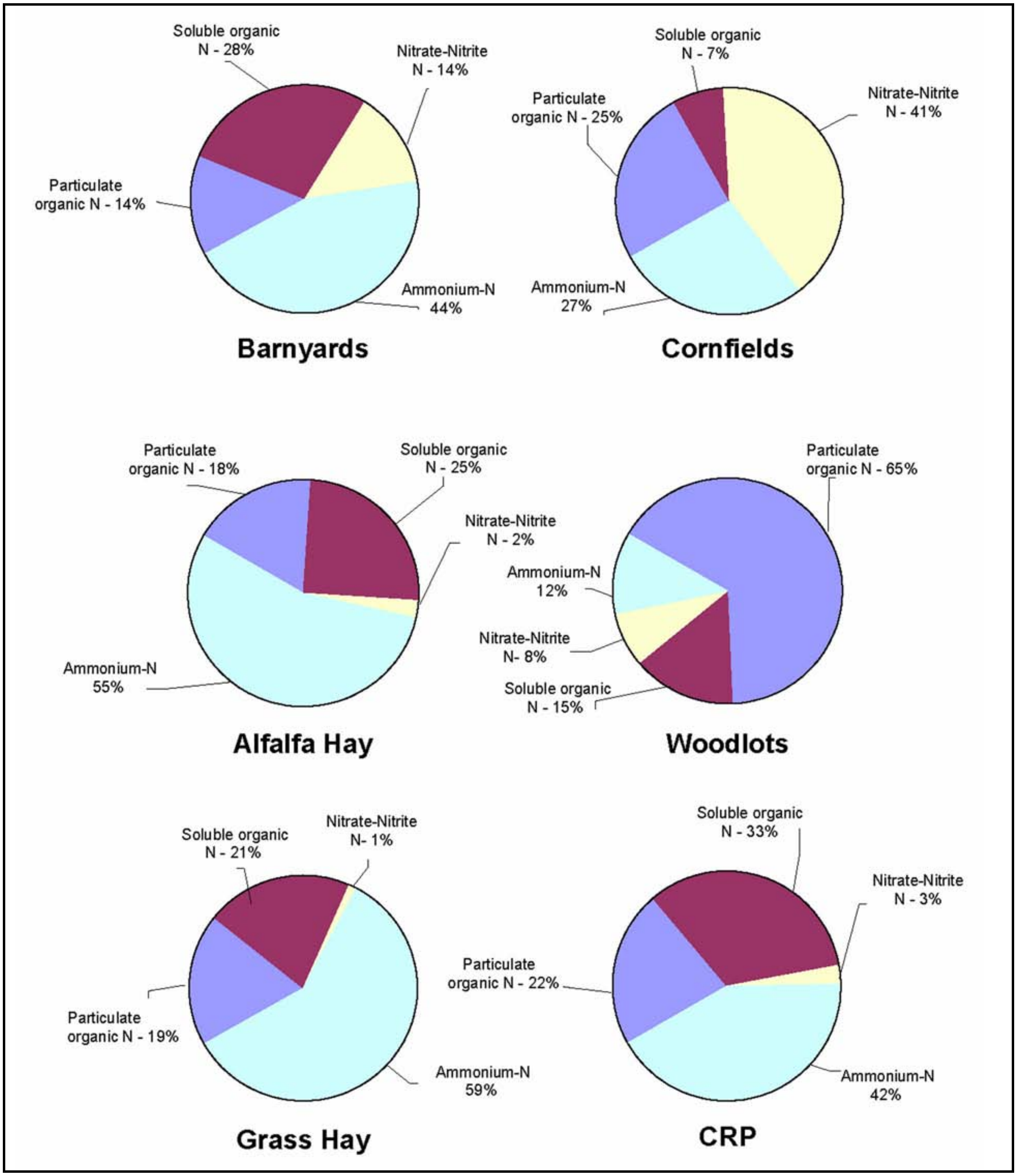

Figure 13. Variations in the mean composition of total nitrogen (N; percent) in the runoff as a function of land use

Land-use variations also appeared to be associated with variations in the concentration of different N forms in the runoff. For instance, PON concentrations were greatest in the runoff from woodlots and cornfields, compared to other land-use categories (Figure 14). NO_3NO_2-N concentrations were greatest in the runoff from cornfields and were substantially higher than concentrations from other land-use categories. In contrast, concentrations of NH_4-N were greatest in barnyard and alfalfa field runoff, compared to other land uses.

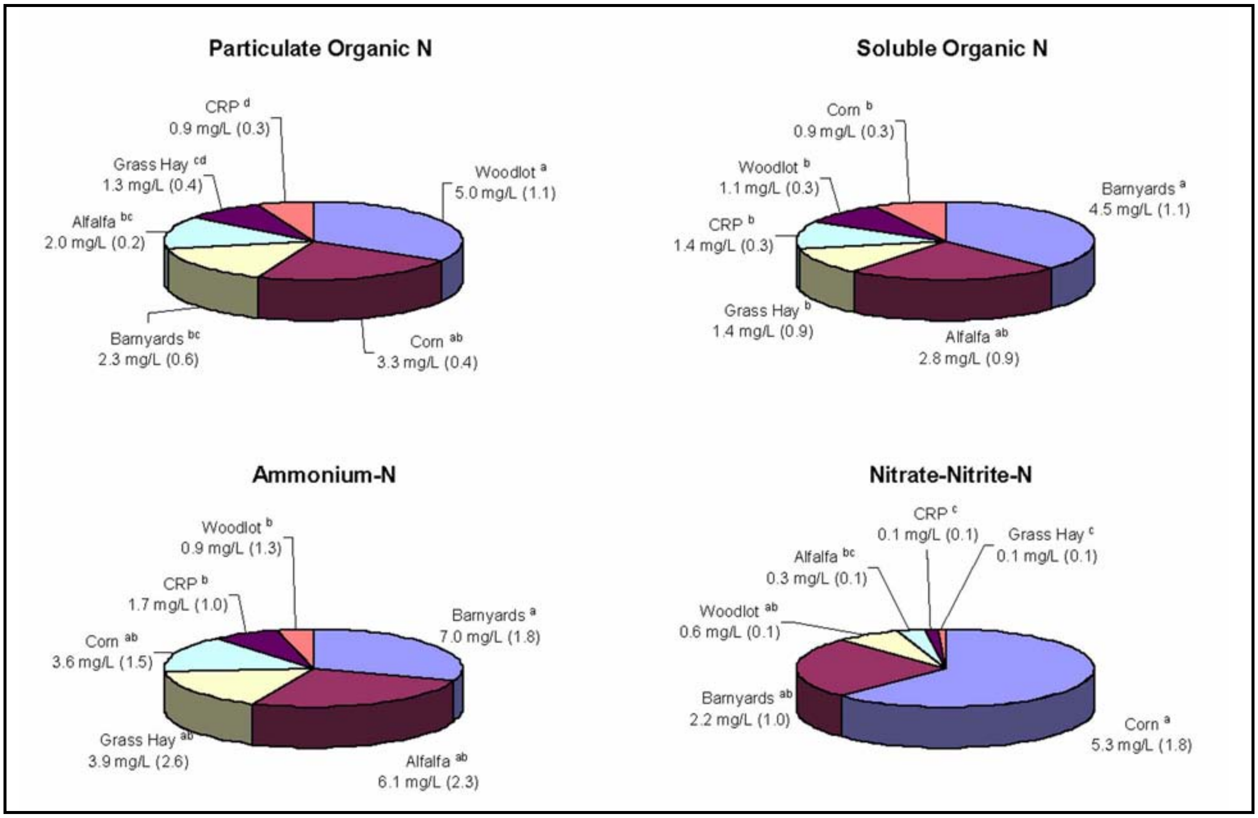

Figure 14. Variations in the mean composition of particulate organic nitrogen (N), soluble organic N, ammonium-N, and nitrate-nitrite-N as a function of land use. Numbers in parentheses represent 1 standard error. Different letters above the means represent significant differences based on Duncan-Waller ANOVA

DISCUSSION: While it was not surprising that barnyard runoff exhibited highest concentrations of soluble P, it was unusual that concentrations of soluble P from alfalfa fields and particulate P from woodlots were unusually high when compared to other land-use practices. Relatively high concentrations of soluble P in the runoff of alfalfa fields in this particular watershed may be attributed to the periodic application of P-rich cow manure on the fields after mowing. Dairy farmers in west-central Wisconsin typically cut and bail alfalfa three to four times in the summer and then apply manure after harvest without incorporating it into the soil via tillage, partly as a means of reducing excess manure stocks. This practice would result in the buildup and exposure to precipitation and runoff of readily solubilized P in the form of manure on the surface soils (Sharpley et al. 1994), similar to patterns observed for runoff concentrations from barnyards. Similarly, although soluble P load did not necessarily increase, Bundy et al.

(2001) found that soluble P concentrations were elevated in the runoff of no-till corn plots spread with manure. They attributed this pattern to enhanced exposure of manure to precipitation in no-till plots versus incorporation of manure into subsurface soil layers in tilled plots.

In contrast to the results of the current study, others have found that wooded regions generally exhibit lower runoff concentrations of P, negligible SRP in the runoff, and lower average ratios of particulate P:soluble P (Vaithiyanathan and Correll 1992), due primarily to canopy and ground cover protection of the soils and conservation of P as biomass and residual organic detritus (Likens and Bormann 1995). In the woodlots examined, runoff of particulate P (and N) was relatively high compared to other land uses, indicating particle erosion during precipitation events. This pattern may have been due to a lack of protective vegetative ground cover under the tree canopy during the summer. While leaf compost was present in the woodlots, its thickness may not have been sufficient to dampen rain intensity and drop energy, particularly during thunderstorms exceeding 20 mm. The majority of the particulate P in the runoff from woodlots was composed of labile and refractory organic particulate forms, which is consistent with the erosion of organic-rich woodland soils.

Cornfields also exhibited high mean runoff concentrations of particulate P forms. This pattern was most likely due to direct exposure of soils to precipitation events and particle erosion (Sharpley et al. 1992). All cornfields examined were tilled, and vegetative ground cover between rows was controlled via herbicide application. In contrast, others have found that runoff can be substantially less under no till or conservation tillage practices (Andraski et al. 1985; Sharpley 1995). Cornfield runoff concentrations also exhibited high concentrations of refractory organic particulate P, which may be attributable to incorporation of composted corn stubble into the surface soils.

CRP land uses exhibited the lowest runoff of both N and P, and soluble forms dominated concentrations in the runoff. Perennial cover protection apparently substantially reduced particle erosion from these fields, as others have also reported (Reddy et al. 1978; Sharpley et al. 1992). Particulate P concentrations in the runoff were also relatively low, compared to cornfield and woodlots, for alfalfa and grass hayfields, which also had perennial cover to dampen rain drop energy during most of the summer. Interestingly, barnyard land uses did not exhibit unusually high particulate P concentrations in the runoff either, even though these soils were directly exposed to precipitation events. Troddened soils in these areas may have been compacted and less susceptible to erosion than in other land-use areas.

The very distinct differences in sorption and equilibrium characteristics of TSS in the runoff were clearly related to differences in land-use practice. Activities in the barnyard and cornfield land uses that promoted incorporation of manure and/or fertilizer into soils appeared to be associated with more elevated concentrations of loosely bound and iron-bound particulate P than TSS from woodlot runoff. These trends suggested increased binding of P on soil sorption sites in excess of crop need for agricultural land-use practices that promoted P subsidies to the soils. In particular, Reddy et al. (1978) found that manure amendments increased the EPC of soils tremendously. Runoff of this TSS could play a very important role in the regulation of soluble P concentrations in receiving waters via equilibrium processes. The very high EPC associated with TSS collected in the runoff from barnyards and cornfields also suggested that TSS from these

land uses could contribute substantially to high soluble P concentrations in receiving waters under conditions of P disequilibrium between particulate and soluble phases via desorption processes. Positive linear relationships between readily exchangeable (i.e., loosely bound and/or iron-bound particulate P) particulate P fractions and soluble P concentrations, the EPC, and the S_o, suggested that these particular fractions played an important role in equilibrium processes and P exchanges between particulate and soluble phases. James et al. (2002, 2004a, 2004b) indicated that equilibrium processes between TSS and aqueous phases were responsible for contributing to high soluble P concentrations in tributaries of the Eau Galle River and the Redwood River, Minnesota. Other studies have found that eroded soils play an important role in P desorption and soluble P concentrations in receiving waters (Sharpley et al. 1981, Klotz 1988).

In contrast, although particulate P runoff concentrations were moderately high for woodlots, sorption characteristics suggested that TSS in the runoff of this land use could act as a sink for soluble P in receiving waters due to the very low EPC. For instance, James et al. (2004a) found that soluble P concentrations were 0.100 mg L^{-1} in the main stem Eau Galle tributaries during high flow events, well above the EPC determined for TSS in the runoff of woodlots. This pattern of low EPC may have been associated with the lack of soil nutrient management and fertilization in these areas. Binding sites on soils in these areas were probably not P saturated and able to scavenge P above a much lower EPC, compared to TSS from barnyard and cornfield runoff. The linear adsorption coefficient was high for TSS collected from the runoff of woodlots, compared to coefficients reported for other soils and aquatic sediments, indicating a high buffering capacity for P under conditions of P disequilibrium.

Overall, agricultural and livestock land-use practices were generally associated with the greatest concentrations of biologically labile P (i.e., soluble P plus labile particulate P) in the runoff, versus the unmanaged woodlot and CRP land uses. Mean Mehlich-3 soil concentrations were also greatest in these land-use areas, suggesting overall relationships between land-use practice, soil P concentrations, and runoff concentrations of labile and soluble P. Others (Pote et al. 1996, 1999; Daniel et al. 1994; Sharpley et al. 1996; Bundy et al. 2001; Andraski and Bundy 2003) have found general relationships between soluble P runoff and variations in soil P concentration due to management for a variety of land-use practices. However, much more information is needed to better define these trends for land uses in the Eau Galle River watershed, as there are many factors other than land-use practice involved in determining runoff concentration., such as P application rate, slope and hydraulic conductivity, and crop cover that need to be considered in P runoff potential (Lemunyon and Gilbert 1993). In addition, variations in the runoff of particulate versus soluble P forms and concentrations need to be examined as a function of land use. For instance, the current results suggested that different forms of P (i.e., soluble versus particulate P) dominated runoff concentrations as a function of land use (i.e., barnyards versus cornfields).

After transport to receiving waters (larger order tributaries and impoundments), soluble P is immediately available for biological uptake. Loosely bound and iron-bound particulate P can become directly available for uptake by biota through kinetic and equilibrium processes (Froelich 1988, Mayer and Gloss 1980, James et al. 2002). Phosphorus from these fractions can also be mobilized after sedimentation via eH and pH reactions (Drake and Heaney 1987, Boers 1991, James et al. 1996). P can be mobilized from labile organic particulate P fractions through

bacterial breakdown and leaching during decomposition (Jensen and Anderson 1992). This fraction also represents polyphosphate stores in bacteria, which can be recycled to the water column for biological uptake (Hupfer et al. 1995).

For nitrogen, soluble forms tended to dominate concentrations from agriculturally managed land uses. High NH_4-N and soluble organic N concentrations in the runoff from barnyards and alfalfa fields were probably linked to mineralization and direct solubilization of organic N in manure deposited over the soil surface. For cornfields, high concentrations of nitrate-nitrite-N in the runoff are most likely due to nitrification of anhydrous ammonia fertilizers incorporated into the soils. Soluble N forms also dominated concentrations in the runoff from grass hayfields, but they were the lowest of the agricultural land-use practices examined.

In contrast, particulate organic nitrogen was the dominant form in the runoff from woodlots, and concentrations were highest from this land-use practice versus the other land uses. Woodlots did not receive agricultural N subsidies in the form of manure or fertilizer; thus, N cycling and transformations were probably tighter in these land uses with N forms being tied up in biomass and compost rather than available as soluble forms associated with the soil. The particulate organic nitrogen running off woodlots is probably refractory in nature and associated with leaf compost. Like phosphorus, cornfields also exhibited a relatively high concentration of particulate organic nitrogen in the runoff, which may represent refractory compost from corn stubble incorporated into the soil.

The results of this study provide unique information on runoff concentrations of labile and refractory N and P components at the field-scale level as a function of different land-use practices. This information can be combined with runoff flow and loading of constituents from the edge of the field to receiving tributaries via hydrologically distributed models in order to better understand nutrient transformations, fluxes, and fate for watersheds exhibiting complex land-use mosaics. In particular, linking concentration trends to land-use practices in hydrologically sensitive areas (i.e., areas susceptible to water saturation and runoff during precipitation; Gburek and Sharpley 1998; Walter et al. 2000, 2001) versus those land uses in areas of low runoff potential will be critical in improving watershed modeling predictive capabilities.

SUMMARY: Agriculturally managed and livestock land-use practices generally exhibited higher concentrations of labile P and soluble N forms in the runoff versus unmanaged land uses (CRP and woodlots). Forms of N and P in the runoff also varied as a function of land use and were related, in large part, to agricultural practices such as row cropping, commercial fertilizer application, and manure inputs. Barnyards and alfalfa fields, which receive manure inputs in this particular watershed, exhibited the highest concentrations of labile P and soluble organic N and ammonium-N in the runoff compared to other land uses. Cornfields exhibited the greatest concentrations of nitrate-nitrite-N in the runoff due to anhydrous ammonia N application and subsequent nitrification. This land-use practice, as well as woodlots, also exhibited high concentrations of particulate forms of N and P in the runoff. For cornfields, lack of vegetative cover due to row cropping and control of weeds via herbicide or cultivation enhanced the particle erosion potential. For woodlots, even though the tree canopy provided top cover to dampen raindrop energy, a lack of vegetative understory contributed to inadequate soil

protection from erosion during strong thunderstorms and heavy precipitation intensity. A better understanding of N and P transformations and speciation in the runoff of different land uses is critical for improving watershed models to more accurately predict nutrient transport and fate in agriculturally managed watersheds.

ACKNOWLEDGMENTS: The authors gratefully acknowledge T. Brunner, M. Daniels, K. Johnson, L Pommier, and M. Weiss of the Eau Galle Aquatic Ecology Laboratory, ERDC, for deployment of RCD's, field sampling, and chemical analyses.

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> James, W. F., Eakin, H. L, Ruiz, C. E., and, Barko, J. W. (2004). "Variations in field-scale nitrogen and phosphorus concentrations in runoff as a function of land-use practice," *SMART Technical Notes Collection*, ERDC/TN SMART-04-6, U.S. Army Engineer Research and Development Center, Vickburg, MS.

REFERENCES

Ameel, J. J., Axler, R. P., and Owen, C. J. (1993). "Persulfate digestion for setermination of total nitrogen and phosphorus in low nutrient waters," *Am. Environ. Lab.*, 8-10.

American Public Health Association. (1998). *Standard methods for the examination of water and wastewater*. 20th ed.

Andraski, B. J., Mueller, D. H., and Daniel, T. C. (1985). "Phosphorus losses in runoff as affected by tillage," *Soil Sci. Soc. Am. J.* 49, 1523-1527.

Andraski, T. W., and Bundy, L. G. (2003). "Relationships between phosphorus levels in soil and in runoff from corn production systems," *J. Environ. Qual.* 32, 310-316.

Boers, P. C. M. (1991). " The influence of pH on phosphate release from lake sediments," *Wat. Res.* 25, 309-311.

Bundy, L. G., Andraski, T. W., and Powell, J. M. (2001) "Management practice effects on phosphorus losses in runoff on corn production systems," *J. Environ. Qual.* 30, 1822-1828.

Daniel, T. C., Sharpley, A. N., Edwards, D. R., Wedepohl, R., and Lemunyon, J. L. (1994). "Minimizing surface water eutrophication from agriculture by phosphorus management," *Soil Water Conserv. Suppl.* 49, 30-38.

Drake, J. C. D., and Heaney, I. (1987) "Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English lake," *Freshwat. Biol.* 17, 513-523.

Froelich, P. N. (1988). "Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism," *Limnol. Oceanogr.* 33,49-668.

Gächter, R., and Meyer, J. S. (1993). "The role of microorganisms in mobilization and fixation of phosphorus in sediments," *Hydrobiologia* 253, 103-121.

Gächter, R., Meyer, J. S., and Mares, A. (1988). "Contribution of bacteria to release and fixation of phosphorus in lake sediments," *Limnol. Oceanogr.* 33, 1542-1558.

Gburek, W. D., and Sharpley, A. N. (1998). "Hydrologic controls on phosphorus loss from upland agricultural watersheds," *J. Environ. Qual.* 27, 267-277.

Hjieltjes, A. H., and Lijklema, L. (1980). "Fractionation of inorganic phosphorus in calcareous sediments," *J. Environ. Qual.* 8, 130-132.

Hupfer, M. R., Gächter, R., and Rüegger, H. (1995). "Polyphosphate in lake sediments: ^{31}P NMR spectroscopy as a tool for its identification," *Limnol. Oceangr.* 40, 610-617.

James, W. F., Barko, J. W., and Eakin, H. L. (2002). Labile and refractory forms of phosphorus in runoff the Redwood River Basin, Minnesota," *J. Freshwat. Ecol.* 17, 297-304.

James, W. F., Barko, J. W., and Field, S. J. (1996) "Phosphorus mobilization from littoral sediments of an inlet region in Lake Delavan, Wisconsin," *Arch. Hydrobiol.* 138, 245-257.

James, W. F., Eakin, H. L., Ruiz, C. E., and Barko, J. W. (2004b). "Soil phosphorus compositional characteristics as a function of land-use practice in the Upper Eau Galle River Watershed, Wisconsin," *Smart Technical Notes Collection*, ERDC/TN SMART-04-5, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

James, W. F., Ruiz, C. E., Barko, J. W., and Eakin, H. L. (2004a). "Longitudinal variations in nitrogen and phosphorus composition and loading characteristics of the Eau Galle River Watershed, Wisconsin," *Smart Technical Notes Collection*, ERDC/TN SMART-04-7, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Jensen, H. S., and Andersen, F. Ø. (1992). "Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes," *Limnol. Oceanogr.* 37, 577-589.

Klotz, R. L. (1988). " Sediment control of soluble reactive phosphorus in Hoxie Gorge Creek, New York," *Can. J. Fish. Aquat. Sci.* 45, 2026-2034.

Lemunyon, J. L., and Gilbert, R. G. (1993). "The concept and need for a phosphorus assessment tool," *J. Prod. Agric.* 6, 483-486.

Likens, G. E., and Bormann, F. H. (1995) *Biogeochemistry of a forested ecosystem.* Springer-Verlag, New York.

Mayer, L. M., and Gloss, S. P. (1980). "Buffering of silica and phosphate in a turbid river," *Limnol. Oceanogr.* 25, 12-25.

Mehlich, A. (1984). "Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant," *Commu. Soil Sci. Plant Anal.* 15, 1409-1416.

Nürnberg, G. K. (1988). "Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments," *Can. J. Fish. Aquat. Sci.* 44, 960-966.

Pant, H. K., and Reddy, K. R. (2001). "Phosphorus sorption characteristics of estuarine sediments under different redox conditions," *J. Environ. Qual.* 30,1474-1480.

Penn, M. R. Auer, M. T., Van Orman, E. L., and Korienek, J. J. (1995). "Phosphorus diagenesis in lake sediments: Investigations using fractionation techniques," *Mar. Freshwat. Res.* 46, 89-99.

Plumb, R. H. (1981). "Procedures for handling and chemical analysis of sediment and water samples," Technical Report EPA/CE-81-1. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Pote, D. H., Daniel, T. C., Nichols, D. J., Sharpley, A. N., Moore, P. A., Miller, D. M., and Edwards, D. R. (1999). "Relationship between phosphorus levels in three utisols and phosphorus concentrations in runoff," *J. Environ. Qual.* 28, 170-175.

Pote, D. H., Daniel, T. C., Sharpley, A. N., Moore, P. A., Edwards, D. R., and Nichols, D. J. (1996) " Relating extractable soil phosphorus to phosphorus losses in runoff," *Soil Sci. Soc. Am. J.* 60, 855-859.

Psenner, R., and Puckso, R. (1988). "Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions," *Arch. Hydrobiol. Biel. Erg. Limnol.* 30:43-59.

Reddy, G. Y., McLean, E. O., Hoyt, G. D., and Logan, T. J. (1978). " Effects of soil, cover crop, and nutrient source on amounts and forms of phosphorus movement under simulated rainfall conditions," *J. Environ. Qual.* 7, 50-54.

Statistical Analysis System (SAS) Institute. (1994) . "SAS/STAT Users Guide, Version 6, 4th ed. SAS Institute, Cary, NC.

Sharpley, A. N. (1995). "Identifying sites vulnerable to phosphorus loss in agricultural runoff," *J. Environ. Qual.* 24, 947-951.

Sharpley, A. N., and Smith, S. J. (1992). "Prediction of bioavailable phosphorus loss in agricultural runoff," *J. Environ. Qual.* 21, 32-37.

Sharpley, A. N., Chapra, S. C., Wedepohl, R., Sims, J. T., Daniel, T. C., and Reddy, K. R. (1994). "Managing agricultural phosphorus for protection of surface waters: Issues and options. *J. Environ. Qual.* 23, 437-451.

Sharpley, A. N., Daniel, T. C., Sims, J. T., and Pote, D. H. (1996). "Determining environmentally sound phosphorus levels," *J. Soil Water Conserv.* 51, 160-166.

Sharpley, A. N., Menzel, R.G., Smith, S.J., Rhoades, E.D., and Olness, A.E. (1981) "The sorption of soluble phosphorus by soil material during transport in runoff from cropped and grassed watershed," *J. Environ. Qual.* 10, 211-215.

Sharpley, A. N., Smith, S. J., Jones, O. R., Berg, W. A., and Coleman, G. A. (1992). "The transport of bioavailable phosphorus in agricultural runoff," *J. Enivron. Qual.* 21, 30-35.

Sharpley, A. N., Troeger, W. W., and Smith, S. J. (1991). "The measurement of bioavailable phosphorus in agricultural runoff," *J. Environ. Qual.* 20, 235-238.

Sims, J. T. (1993). "Environmental soil testing for soil phosphorus," *J. Prod. Agric.* 6, 501-507.

Viahiyanathan, P., and Correll, D. L. (1992). " The Rhode River watershed: Phosphorus distribution and export in forest and agricultural soils," *J. Environ. Qual.* 21, 280-288.

Walter, M. T., Brooks, E. S., Walter, M. F., and Steenhuis, T. S. (2000). "Hydrologically sensitive areas: Variable source area hydrology implications for water quality risk assessment," *J. Soil Water Conserv.* 3, 277-284.

Walter, M. T., Brooks, E. S., Walter, M. F., Steenhuis, T. S., Scott, C. S., and Boll, J. (2001). "Evaluation of soluble phosphorus loading from manure-applied fields under various spreading strategies," *J. Soil Water Conserv.* 56, 329-336.